

NOVEL APPROACH TO THE PRODUCTION OF GRAPHITE FROM ANTHRACITE

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INTRODUCTION

Currently the carbon/graphite industry uses petroleum coke as the main filler constituent in the manufacture of graphite. Anthracite has been successfully used as fillers for amorphous carbon electrodes, but has not been used in the production of graphite electrodes because of its non-graphitizable structure. Creating a cost-effective graphitizable anthracite, which would have characteristics to be a viable substitute for petroleum coke, would help find an alternative use for Pennsylvania's anthracite and reduce the industry's dependence on petroleum. In the present project, a unique approach to make graphite from anthracite, focused on modifying anthracite's precursor structure by adding a hydrogen-donating substance, has been conducted. This approach is based on two major hypotheses. First, a supply of donatable or transferable hydrogen is needed for the hydrogen-deficient anthracite structure to disrupt crosslink formation between aromatic structures within the coal. Secondly, an aromatic liquid medium is needed to help prevent electronic interactions between aromatic structures and provide the fluidity necessary for aromatic realignment into the graphite structure.

Several hydrogen donors were investigated. 9,10-Dihydroanthracene showed the best ability to donate hydrogen to anthracite and also formed a highly anisotropic anthracene coke in the process. Phenanthrene was selected as the aromatic liquid medium. Both anthracene and phenanthrene have been found to be highly graphitizable [1]. Although hydrogen was successfully donated to the anthracite, the hydrogen donation is believed to have only occurred at the surface and did not affect the internal structure of the coal. Previously treated samples showed good anisotropic character and approached the interlayer spacing of the graphite structure upon heating to graphitization temperatures, but the graphitized anthracites did not show any layering characteristics or crystalline height, L_c [2]. Rouzand and others have found the structure and shape of the initial porosity and flow microstructures of the raw anthracite to be a major factor in the extent of graphitization of anthracite [3]. Because of the dependence of graphitizability on pore structure and the resistance of the internal coal structure to hydrogen donation, six anthracites were studied to determine their pore characteristics. Three of the anthracites, representing a variety of pore characteristics, were then selected to investigate the hydrogenation and subsequent graphitization of the anthracites treated with dihydroanthracene.

EXPERIMENTAL

Six anthracites from various mines in the eastern Appalachian coal region were obtained from the Penn State Coal Sample Bank and Data Base. All of the pore characterization was carried out on 60–100 mesh samples. Helium pycnometry, using a Quantachrome Multipycnometer MVP-1, at room temperature was used to find true densities, weight per unit volume of the pore-free solid. Mercury porosimetry (Quantachrome Autoscan Mercury Porosimeter) was used to obtain the particle density, the weight of a unit volume of solid including pores. Values at 60 psi were taken since interparticle voids are more or less completely filled with mercury at this pressure. The volume percent of open porosity was then calculated from these two density measurements. Macro- and mesopore size distributions were also determined from mercury porosimetry. Both nitrogen and carbon dioxide surface areas were determined, at -196°C and 0°C respectively, using a Quantachrome Autosorb-1 automated gas adsorption system. Nitrogen surface areas were calculated using the BET equation. However, the adsorption of N_2 in microporous coals is severely limited and gives appreciably lower values. Carbon dioxide can reach much more of the coals' internal porosity [5]. The Carbon dioxide surface area was calculated using the DR method. Both BET and DR plots showed a greater than 99.5% correlation to a straight line fit. Nitrogen pore volumes were also obtained. Three anthracites were selected for subsequent experimentation: DECS-21, PSOC-1468, and PSOC-1461.

Anthracite samples, -60 mesh, were charged in 20mL capacity stainless steel microautoclave reactors with a mixture of 75% 9,10-dihydroanthracene and 25% phenanthrene, in a 1:2 coal-to-donor ratio. Ratios of higher amounts of dihydroanthracene mixture were also run. Reactions were carried out under 1000 psi nitrogen pressure in a fluidized sand bath. Reactors were continuously agitated to keep the reactants well mixed. A temperature-controlled heat treatment was used: 3h initial hold at 200°C , temperature increased to 550°C at the rate of 5°C/h , and a final hold at 550°C for 2 h. The products were extracted with tetrahydrofuran (THF) for 24h. Optical microscopy samples were then made of the THF-insoluble material and analyzed under a polarized light microscope (Nikon microphot-FXA) with 35mm camera and video ports. Optical micrographs of typical areas were taken. Samples were further heat treated at 1500°C for 4h and observed optically then graphitized. Graphitization was conducted at the Carbide/Graphite Group Inc. in St. Marys, PA using an industrial induction furnace. Samples were heated to 2700°C and 2900°C for 5 hours in purified graphite crucibles. Graphitized anthracite samples were analyzed using optical microscopy again and x-ray diffraction, SCINTAG/USA PAD-V diffractometer with $\text{CuK}\alpha$ radiation. Calculations of the quality and the amount of the sample in the graphite structure were made using X-ray data.

RESULTS and DISCUSSION

The open porosity of the six raw anthracites was calculated from helium and mercury densities and are recorded in Table 1. The mercury densities were calculated using the Washburn equation and all of the densities ranged from 1.53 to 1.63 g/cm³. These values are about 0.2 g/cm³ higher than Mahajan and Walker's results for anthracites. This difference can be explained by the fact Mahajan used de mineralized samples and a smaller particle size fraction, 40–70 mesh [6]. Helium densities ranged from 1.56 to 1.65 g/cm³, except for PSOC-1461 which had a considerably higher density of 1.79 g/cm³. Anthracites have shown the presence of some porosity closed to helium [7]. Curtz and Hirsh also used X-ray studies of anthracites to show interlayer spacings corresponding to true densities of 2.0 g/cm³, as compared to helium densities of 1.5 g/cm³ [8]. PSOC-1461 possibly had a much smaller amount of this porosity closed to helium and therefore gave a much higher density value. Volume percent open porosity values were very small, less than 5.5% with exception of PSOC-1461. PSOC-1468 showed the smallest volume percent of 1.3%.

Surface areas for nitrogen and carbon dioxide are also recorded in Table 1. Considerable care was taken to outgas the coals for over 24 hours due to the difficulties in removing moisture from the microporosity. The microporosity of these anthracite samples is clearly seen by the very low nitrogen surface areas and high carbon dioxide surface areas. Nitrogen surface areas ranged from 0.62 to 4.56 m²/g and were expected to correspond to the amount of open porosity calculations, but PSOC-1467, 1461 and 867 did not show such relationship. Carbon dioxide surface areas were much higher since CO₂ can reach more of the coal's porosity and ranged from 320 and 460 m²/g. DECS-21 showed the largest CO₂ surface area while PSOC-1461 had the smallest surface area.

The very small pore volumes recorded for nitrogen adsorption, Table 2, also point to a very microporous structure. Total pore volumes ranged from 0.9 to 4.6 × 10⁻³ cm³/g. Mercury porosimetry which was taken to 60,000 psi showed only an order of magnitude higher total pore volumes. The mercury intrusion results are also summarized in Table 2. The mercury pore volumes corresponded to the nitrogen volumes except for PSOC-1467. Mercury pore size distributions showed only a very small fraction of macroporosity. Mercury porosimetry can not measure the microporosity. The meso and macroporosity are of interest because this is the porosity which would be intruded by the hydrogen donor. The extensive amount of microporosity and lack of open porosity help point to the difficulties of gaining hydrogen transfer throughout the anthracite structure. There could be many reasons for some of the discrepancies seen in the pore characterization data. Smith and others listed some of the major reasons for the complications in pore characterization, of which the complex pore shapes and connectivities, along with chemical and physical heterogeneities, could easily be reasons for the difficulties in coal characterization [9].

Using the above data, three anthracites were selected for their varying pore characteristics to be further treated with the dihydroanthracene. The proximate and ultimate analyses for these three anthracites is shown in Table 3. DECS-21 was selected for its high CO₂ and N₂ surface area and mid-ranged open porosity. PSOC-1468 was selected for its low open porosity, small N₂ surface area, mid-ranged CO₂ surface area, and low total pore volume with the highest fraction of macroporosity. PSOC-1461 was selected for its high open porosity, and small CO₂ surface area. Table 3 also shows these three samples have very different ash, carbon, hydrogen and oxygen contents.

After samples were reacted, optical micrographs were taken. All three anthracites showed similar optical behavior at this stage; therefore, only the micrographs for DECS-21 (Figure 1) will be discussed. Micrograph (a) shows the anthracite heated to 550 °C without hydrogen donor. The anthracite retains its ridged shape and shows a small amount of inherent anisotropy. Micrographs (b and c) are of the coal reacted with dihydro-anthracene at different magnifications. Micrograph (b) shows how the dihydro-anthracene has been converted to an anisotropic coke which surrounds and binds the anthracite particles together. However, no structural change in the anthracite particles can be seen at this stage. Micrograph (c) shows better the flow domains produced by the mesophase development of the anthracene. This micrograph also shows a very good binding of the anthracene coke to the anthracite. In future work, optical micrographs will be taken of samples heated to 1500 °C and after graphitization to observe if any of the anthracene is imbibed into the anthracite particle and if any structural change of the anthracite has occurred. In addition, X-ray diffraction will be used to classify the quality of the graphite using interlayer spacing and L_c, and to determine the amount of graphitic material present using intensity data.

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Table 1. Physical properties of untreated anthracite samples.

| Sample | He Density (g/cm ³) | Hg Density (g/cm ³) | Open Porosity volume % | Surface Area (m ² / g) | |
|-----------|------------------------------------|------------------------------------|------------------------------|--------------------------------------|-----------------|
| | | | | N ₂ | CO ₂ |
| DESC-21 | 1.615 | 1.530 | 5.3 | 4.13 | 460.4 |
| PSOC-1468 | 1.653 | 1.631 | 1.3 | 0.92 | 392.8 |
| PSOC-1467 | 1.563 | 1.528 | 2.2 | 4.56 | 379.7 |
| PSOC-1461 | 1.794 | 1.549 | 13.6 | 2.56 | 319.7 |
| PSOC-1456 | 1.562 | 1.537 | 1.6 | 1.31 | 425.8 |
| PSOC-867 | 1.635 | 1.562 | 4.5 | 0.62 | 320.4 |

Table 2. Nitrogen adsorption pore volume and mercury porosimetry.

| Sample | Carbon wt% (daf) | Total Pore Volume x10 ⁻³ (cm ³ /g) | Hg Porosimetry | | |
|-----------|---------------------|---|---|---|--|
| | | | Total Pore Volume x10 ⁻³ (cm ³ /g) | Mesopore Volume x10 ⁻³ (cm ³ /g) | Macropore Volume x10 ⁻³ (cm ³ /g) |
| DESC-21 | 90.33 | 3.7 | 40.1 | 39.2 | 0.9 |
| PSOC-1468 | 95.36 | 1.0 | 28.9 | 27.7 | 1.2 |
| PSOC-1467 | 93.29 | 4.6 | 86.0 | 82.2 | 2.7 |
| PSOC-1461 | 93.47 | 4.2 | 48.2 | 48.0 | 0.2 |
| PSOC-1456 | 94.56 | 1.5 | 31.9 | 31.6 | 0.3 |
| PSOC-867 | 95.07 | 0.9 | 27.9 | 27.9 | 1.1 |

Table 3. Analysis of anthracite samples selected.

| Sample Seam | DECS-21 Lykens Valley | PSOC-1468 Buck Mountain | PSOC-1461 Mammoth |
|--|--------------------------|----------------------------|----------------------|
| <u>Proximate Analysis</u> (as rec.) | | | |
| % Moisture | 3.99 | 4.51 | 3.06 |
| % Ash | 10.71 | 6.52 | 23.44 |
| % Volatile | 4.33 | 3.49 | 3.89 |
| % Fixed Carbon | 80.97 | 85.48 | 69.61 |
| <u>Ultimate Analysis (dry)</u> | | | |
| % Ash | 11.15 | 6.83 | 24.14 |
| % Carbon | 80.26 | 88.85 | 70.87 |
| % Hydrogen | 3.56 | 1.29 | 1.45 |
| % Nitrogen | 0.71 | 0.78 | 0.87 |
| % Total Sulfur | 0.50 | 0.49 | 0.74 |
| % Oxygen (diff) | 3.82 | 1.76 | 0.89 |
| Atomic H/C (dmmf) PARR | 0.5328 | 0.1744 | 0.2457 |
| Atomic O/C (dmmf) | 0.0295 | 0.0121 | 0.0031 |

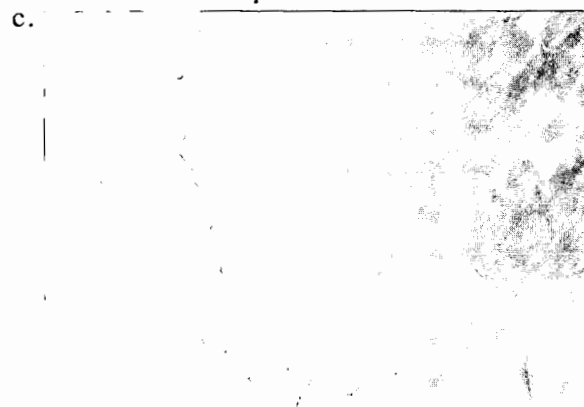
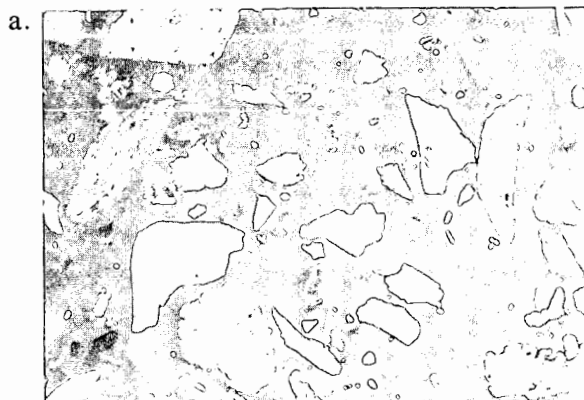


Figure 1. Polarized optical micrographs of anthracite, DESC-21, heated to 550 °C; (a) untreated,, 100 X; (b) coal and 9,10-dihydroanthracene, 100X; (c) coal and 9,10-dihydroanthracene, 400X.